

PB87-182838

Natural Gradient Experiment on
Solute Transport in a Sand Aquifer
3. Retardation Estimates and
Mass Balances for Organic Solutes

Stanford Univ., CA

Prepared for

Robert S. Kerr Environmental Research Lab.
Ada, OK

1986



TECHNICAL REPORT DATA <i>(Please read Instructions on the reverse before completing)</i>		
1. REPORT NO. EPA/600/J-86/330	2.	3. PB87-182838
4. TITLE AND SUBTITLE A NATURAL GRADIENT EXPERIMENT ON SOLUTE TRANSPORT IN A SAND AQUIFER. 3. Retardation Estimates and Mass Balances for Organic Solutes (Journal Version)	5. REPORT DATE 1986	
	6. PERFORMING ORGANIZATION CODE	
7. AUTHOR(S) Paul V. Roberts, Mark N. Goltz, and Douglas M. Mackay	8. PERFORMING ORGANIZATION REPORT NO.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Civil Engineering Stanford University Stanford, CA	10. PROGRAM ELEMENT NO. CBWD1A	
	11. CONTRACT/GRANT NO. CR-808851	
12. SPONSORING AGENCY NAME AND ADDRESS Robert S. Kerr Environmental Research Lab. - Ada, OK U.S. Environmental Protection Agency Post Office Box 1198 Ada, OK 74820	13. TYPE OF REPORT AND PERIOD COVERED Journal Article	
	14. SPONSORING AGENCY CODE EPA/600/15	
15. SUPPLEMENTARY NOTES Published in WATER RESOURCES RESEARCH, 22(13):2047-2058, December 1986.		
16. ABSTRACT The long-term behavior of five organic solutes during transport over a period of 2 years in ground water under natural gradient conditions was characterized quantitatively by means of moment estimates. Total mass was conserved for two of the organic compounds, carbon tetrachloride and tetrachloroethylene, while the total mass declined for three other compounds, bromoform, 1,2-dichlorobenzene, and hexachloroethane. The declines in mass for the latter three compounds are interpreted as evidence of transformation of the compounds. Retardation factors for the organic solutes, relative to chloride, ranged from 1.5 to 9.0, being generally greater for the more strongly hydrophobic compounds. The retardation is attributed to sorption. The apparent retardation factor increased markedly for all compounds over the duration of the experiment, by as much as 150%. Results from temporal and spatial sampling were in good agreement when compared at the same scale of time and distance.		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
18. DISTRIBUTION STATEMENT RELEASE TO THE PUBLIC.	19. SECURITY CLASS (This Report) UNCLASSIFIED.	21. NO. OF PAGES 13
	20. SECURITY CLASS (This page) UNCLASSIFIED.	22. PRICE

A Natural Gradient Experiment on Solute Transport in a Sand Aquifer

3. Retardation Estimates and Mass Balances for Organic Solutes

PAUL V. ROBERTS, MARK N. GOLTZ, AND DOUGLAS M. MACKAY

Department of Civil Engineering, Stanford University, California

The long-term behavior of five organic solutes during transport over a period of 2 years in groundwater under natural gradient conditions was characterized quantitatively by means of moment estimates. Total mass was conserved for two of the organic compounds, carbon tetrachloride and tetrachloroethylene, while the total mass declined for three other compounds, bromoform, 1,2-dichlorobenzene, and hexachloroethane. The declines in mass for the latter three compounds are interpreted as evidence of transformation of the compounds. Retardation factors for the organic solutes, relative to chloride, ranged from 1.5 to 9.0, being generally greater for the more strongly hydrophobic compounds. The retardation is attributed to sorption. The apparent retardation factor increased markedly for all compounds over the duration of the experiment, by as much as 150%. Results from temporal and spatial sampling were in good agreement when compared at the same scale of time and distance.

INTRODUCTION

The long-term behavior of trace organic solutes in groundwater has become a subject of great interest in connection with investigation of environmental releases of hazardous chemicals and wastes. Synthetic organic chemicals have been widely observed as ground water contaminants and are believed to persist over long periods, to provide a data base suitable for documenting the behavior of organic contaminants under natural conditions and for demonstrating the significance of fundamental processes governing solute behavior, a long-term experiment was undertaken at Canadian Forces Base, Borden, Ontario [Mackay *et al.*, this issue]. The study site was in close proximity to the scene of a previous solute transport investigation at Borden that focused on chloride as a tracer [Sudicky *et al.*, 1983].

The general objective of this transport experiment was to improve understanding of the principles governing solute transport under natural conditions in the subsurface, with emphasis on the behavior of halogenated organic compounds at trace concentration levels over a time scale measured in years [Mackay *et al.*, this issue]. Previous papers in this series have dealt with the design and preliminary assessment of the experiment [Mackay *et al.*, this issue] and with the detailed moment analysis of the conservative tracers, chloride and bromide [Freyberg, this issue]. This paper deals specifically with field evidence of retardation and transformation of halogenated organic solutes. The organic solutes investigated were carbon tetrachloride, CCl_4 (CTET); bromoform, CHBr_3 (BROM); tetrachloroethylene, $\text{Cl}_2\text{C}=\text{CCl}_2$ (PCE); 1,2-dichlorobenzene, $\text{C}_6\text{H}_4\text{Cl}_2$ (DCB); and hexachloroethane, C_2Cl_6 (HCE). Data are presented for a 2-year period, August 1982 to August 1984, during which samples were taken and analyzed for the organic solutes as well as the conservative tracers.

A specific goal was to assess the constancy, over space and time, of the retardation factors (groundwater velocity divided by solute velocity). A corollary goal was to compare the retardation estimates obtained from time-series sampling at particular points with estimates based on periodic, high-resolution spatial sampling. From the observed retardation factors, the

sorption behavior of the several solutes has been inferred and compared to results of laboratory experiments [Curtis *et al.*, this issue]. Evidence of transformation of the organic compounds was sought by evaluating changes in mass over the time span of the observations.

APPROACH

The experimental design and implementation have been described elsewhere [Mackay *et al.*, this issue]. To recapitulate briefly, a uniform solution of five organic solutes and two inorganic tracers was introduced into the saturated zone of a sand aquifer in the form of an approximately rectangular prism [Mackay *et al.*, this issue, Figure 6]. Thereafter the solutes were monitored as they migrated under the influence of the natural hydraulic gradient, which at the Borden site results in an average linear ground water velocity of approximately 0.09 m/day.

Retardation factors were estimated in two ways: (1) by comparing average travel times estimated from breakthrough responses for the organic solutes with the travel time of chloride, based on time-series sampling at discrete points, and (2) by comparing the velocities of the organic solutes with that of the chloride tracer, based on analyses of samples taken from a three-dimensional sampling array at a particular time. The former is termed breakthrough sampling, and the latter is referred to as spatial snapshot or synoptic sampling. In interpreting the spatial data, the method of moment calculations described by Freyberg [this issue] was employed. The zeroth moment of the spatial concentration data was used to estimate the mass in solution, and the first moment was used to estimate the position of the center of mass. The errors implicit in the sampling, analysis, and data interpretation are discussed by Mackay *et al.* [this issue] and Freyberg [this issue].

In the present paper, organic solute behavior is compared to that of chloride, assuming the latter to be a nonreactive tracer. A previous paper [Freyberg, this issue] has demonstrated that chloride and bromide behaved similarly in all important respects, and thus the bromide data are omitted from this paper for simplicity.

TIME-SERIES SAMPLING RESULTS

Concentration Observations

Results of time-series samplings (breakthrough responses) are presented for three individual monitoring points, designa-

Copyright 1986 by the American Geophysical Union.

Paper number 5W4219.
0043-1397/86/005W-4219\$05.00

NTIS is authorized to reproduce and sell this report. Permission for further reproduction must be obtained from the copyright owner.

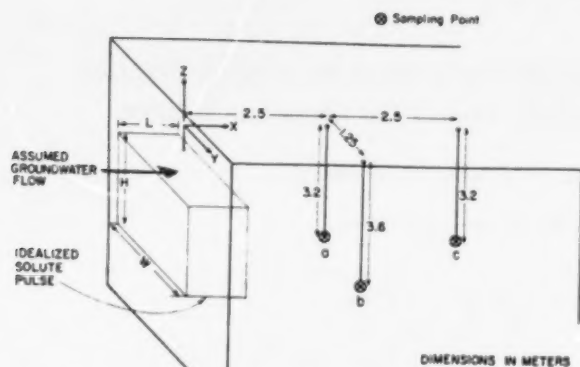


Fig. 1. Configuration of the injected pulse and the time series sampling points. Zone initially permeated by injected water is conceptualized as a rectangular prism with dimensions $L = 3.2$ m, $H = 1.6$ m, and $W = 6$ m.

ted by their x , y , and z coordinate positions (in meters) relative to ground level at the center of the injection zone: a, 2.5, 0.0, -3.20; b, 2.5, 1.25, -3.62; and c, 5.0, 0.0, -3.26. These points were located 2.5, 2.5, and 5.0 m from the transverse axis of the injected solute pulse (Figure 1), and were within the boundaries of the passing solute plumes [Mackay *et al.*, this issue; Freyberg, this issue].

The concentration histories for chloride and two of the

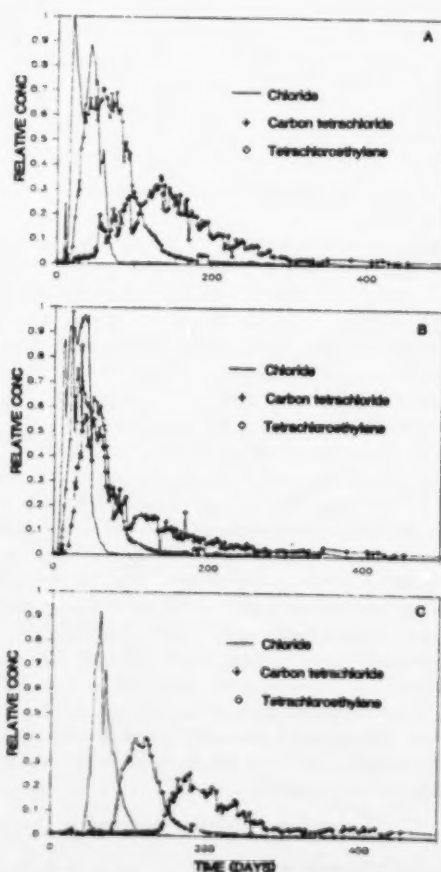


Fig. 2. Breakthrough responses for chloride, carbon tetrachloride, and tetrachloroethylene at time-series sampling points a, b, c.

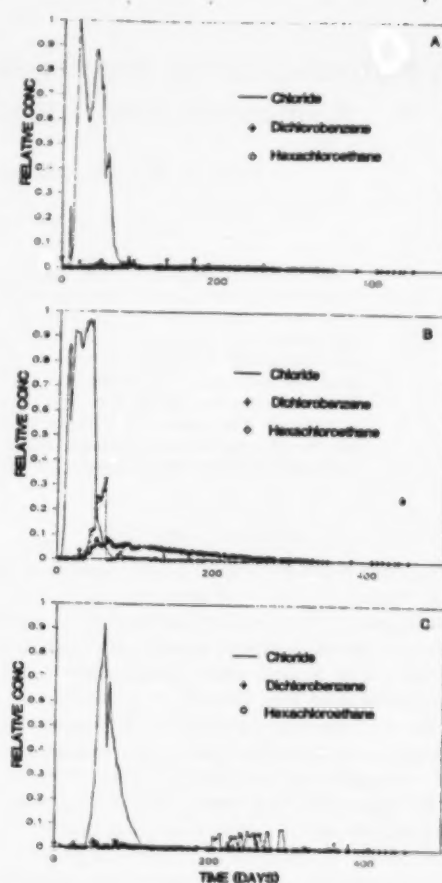


Fig. 3. Breakthrough responses for dichlorobenzene and hexachloroethane at time-series sampling points a, b, and c. Chloride data from Figure 2 are repeated here to facilitate comparison.

organic solutes, carbon tetrachloride and tetrachloroethylene, are depicted in Figure 2 at each sampling point, a, b, and c. The record consists of approximately 180 samples taken over a 16-month period, August 1982 to December 1983. The concentration data in Figure 2 are normalized to the following average injection solution concentrations, C_0 : chloride, 892 mg/L; carbon tetrachloride, 30.7 $\mu\text{g/L}$; and tetrachloroethylene, 30.2 $\mu\text{g/L}$ [Mackay *et al.*, this issue]. The data for bromoform ($C_0 = 32.1$ $\mu\text{g/L}$) are omitted from Figure 2 for clarity, as its behavior coincides so closely with that of carbon tetrachloride at these monitoring points that it would be difficult to distinguish them.

Qualitatively, the concentration histories in Figure 2 display several properties anticipated prior to the experiment based on equilibrium chromatographic theory [Lapidus and Amundson, 1952; Vermeulen and Hiester, 1952; Hashimoto *et al.*, 1964; Lindstrom *et al.*, 1967; Yu *et al.*, 1984]: (1) chloride, the conservative tracer, arrives first at any monitoring point; (2) the arrivals of organic solutes are retarded to varying degrees; and (3) assuming steady flow and coincident initial distributions of solute, the areas under the time-concentration curves are approximately equal. The relative concentrations are highest for monitoring points a and b because these points were nearer to the source than was point c. The most rapid responses (those of chloride and carbon tetrachloride at the closest points, a and b) exhibit the broad peak feature which

TABLE 1. Time-Series Data Summary

Monitoring Point*	Solute	Average Travel Time, days	Retardation Factor	Absolute Integral Area, days	Relative Integral Area†
a (2.5, 0.0, -3.2)	chloride	37.6	1.0	34.2	1.0
	carbon tetrachloride	67.3	1.8	52.7	1.5
	bromoform	67.7	1.8	46.1	1.3
	tetrachloroethylene	145.0	3.9	47.6	1.4
	dichlorobenzene	103.0	2.7	1.4	0.04
	hexachloroethane	166.0	4.4	1.7	0.05
b (2.5, 1.25, -3.62)	chloride	30.4	1.0	35.2	1.0
	carbon tetrachloride	48.2	1.6	43.0	1.2
	bromoform	45.6	1.5	39.3	1.1
	tetrachloroethylene	83.0	2.7	47.4	1.3
	dichlorobenzene	55.0	1.8	5.6	0.16
	hexachloroethane	122.0	4.0	9.6	0.27
c (5.0, 0.0, -3.26)	chloride	66.2	1.0	23.1	1.0
	carbon tetrachloride	119.3	1.8	24.9	1.1
	bromoform	122.3	1.8	22.3	1.0
	tetrachloroethylene	217.0	3.3	29.4	1.3
	dichlorobenzene	245.0	3.7	5.1	0.22
	hexachloroethane	81.0	1.2	1.0	0.04

*Coordinate position (x, y, z) in meters is given in parentheses.

†Normalized to chloride integral area at same sampling point.

would be the expected near-field response to a broad finite pulse assuming advective/dispersive transport [Hunt, 1978].

The breakthrough responses for two additional organic compounds, dichlorobenzene ($C_0 = 332 \mu\text{g/L}$) and hexachloroethane ($C_0 = 19.6 \mu\text{g/L}$), are shown in Figure 3 for the same three monitoring points: Figure 3a corresponds to Figure 2a, Figure 3b to Figure 2b, and Figure 3c to Figure 2c. The relative concentrations of dichlorobenzene and hexachloroethane (Figure 3) are clearly much smaller than those of chloride and the other organic solutes (Figure 2). Indeed, the hexachloroethane relative concentration does not exceed 0.1 at any time at any of the three monitoring points, and the dichlorobenzene relative concentration exceeds 0.1 only at point b, which is nearest the plume centroid path, and where hexachloroethane also reached higher relative concentration than at points a and c. The behavior of dichlorobenzene at point b is anomalous, compared to other solutes at the same point (Figures 2 and 3) in that the concentration declined precipitously at approximately $t = 60$ days, and thereafter did not exceed trace levels. At points a and c, the occurrence of both dichlorobenzene and hexachloroethane was sporadic and restricted to trace levels.

Retardation and Relative Mass

The integral properties of the concentration histories (Figures 2 and 3) are summarized in Table 1. The average travel time of a particular solute i at a particular point is calculated as

$$\bar{t}_i = \frac{\sum_{j=1}^n (C_{ij}/C_{i0})t_j}{\sum_{j=1}^n (C_{ij}/C_{i0})} \quad (1)$$

The retardation factor is defined as the average travel time relative to that of chloride

$$R_i = \bar{t}_i / \bar{t}_{\text{chloride}} \quad (2)$$

The absolute integral area is estimated as

$$A = \sum_{j=1}^n (C_{ij}/C_{i0})\Delta t \quad (3)$$

and the relative integral area (A_{rel}) is the value normalized to that of chloride at the same monitoring point.

The ranges of retardation at the three monitoring points (Table 1) are as follows: carbon tetrachloride, 1.6 to 1.8; bromoform, 1.5 to 1.8; tetrachloroethylene, 2.7 to 3.9; dichlorobenzene, 1.8 to 3.7; and hexachloroethane, 1.2 to 4.4. The estimates for dichlorobenzene and hexachloroethane are of questionable accuracy, owing to their erratic behavior and very low concentration levels. For the latter two compounds, the retardation factors estimated at point b (1.8 and 4.0 for dichlorobenzene and hexachloroethane, respectively) are considered the most reliable from the viewpoint that the highest relative concentrations were observed at that point. However, the dichlorobenzene retardation estimate at point b may be negatively biased by truncation of the plume's trailing edge resulting from transformation, as discussed below.

The estimates of relative area give a consistent picture. The relative amounts of carbon tetrachloride (1.27 ± 0.21), bromoform (1.13 ± 0.15), and tetrachloroethylene (1.33 ± 0.06) slightly exceed unity at all three points, indicating that the observed amounts of these compounds are at least as great as can be accounted for by the mass introduced along the flow path intercepted by the monitoring point. Of the three compounds, only tetrachloroethylene's relative mass is significantly greater than unity, however, with 95% confidence intervals on its relative integral area of $1.18 < A_{rel} < 1.48$. The relative integral areas for dichlorobenzene and hexachloroethane are 0.14 ± 0.09 and 0.12 ± 0.13 , respectively, both significantly less than unity. This indicates a deficiency of mass observed over time at the sampling points for the latter two compounds, compared to the masses introduced.

SYNOPTIC SAMPLING RESULTS

Overview of Data

A total of 13 synoptic data sets were obtained for tracers and for organic solutes over the 2-year period, and a total of 10,192 and 9,343 samples were analyzed for chloride/bromide and organic solutes, respectively [Mackay et al., this issue].

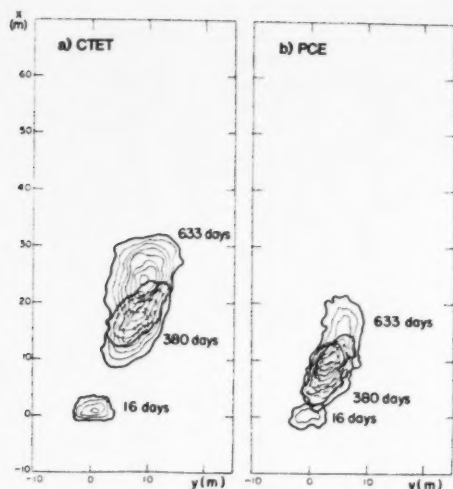


Fig. 4. Movement and spreading of the carbon tetrachloride (CTET, frame a) and tetrachloroethylene (PCE, frame b) plumes. The contour intervals depicted for CTET and PCE are $0.1 \mu\text{g/L}$ beginning at an outer contour of $0.1 \mu\text{g/L}$ (days 380 and 633) and $2 \mu\text{g/L}$ beginning at an outer contour of $2 \mu\text{g/L}$ (day 16).

The first samplings were conducted simultaneously for tracers and organic solutes; the last six samplings were conducted separately for tracers and organic solutes to accommodate the large numbers of samples in the analytical laboratory.

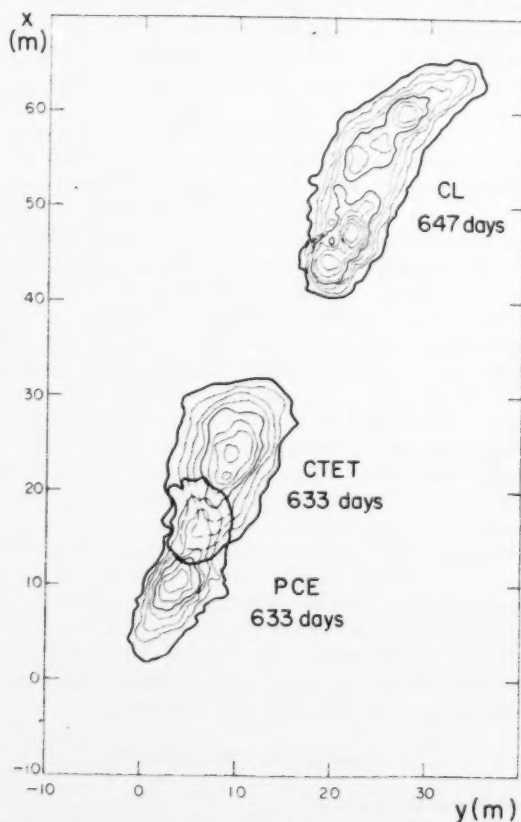


Fig. 5. Chromatographic separation of plumes: chloride (CL, 647 days); carbon tetrachloride (CTET, 633 days); and tetrachloroethylene (PCE, 633 days). Contour interval depicted for CL is 5 mg/L beginning at an outer contour of 10 mg/L . Contour intervals depicted for CTET and PCE are $0.1 \mu\text{g/L}$ beginning at an outer contour of $0.1 \mu\text{g/L}$.

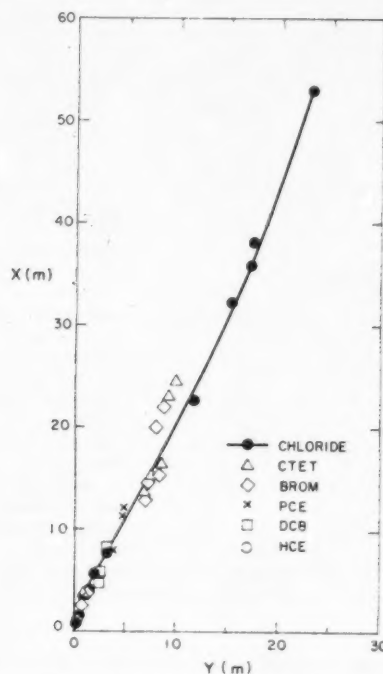


Fig. 6. Paths of plume centers of mass.

Description of Plume Movement

The initial spatial distributions of organic solutes were similar to that of chloride [Mackay *et al.*, this issue, Figure 7]. The organic solute plume movement can be illustrated by means of two-dimensional contours (i.e., in the x - y plane) of depth-averaged concentration values, obtained in the manner described by Freyberg [this issue]. Examples are shown in Figures 4 and 5. In Figure 4 the movement and spreading of the carbon tetrachloride and tetrachloroethylene plumes are depicted. In Figure 5 the positions of the chloride, carbon tetrachloride, and tetrachloroethylene plumes during the twenty-second month of the experiment are shown. The substantial spreading of the plumes in the longitudinal direction is apparent in Figures 4 and 5. Also apparent is the separation of the chloride plume from the more slowly moving organic plumes.

Despite the separation of the plumes, the direction of movement of the organic plumes did not differ from that of chloride. The colinearity of plume movement is illustrated in Figure 6, in which the horizontal positions of the plume centers of mass are plotted. The positions of the organic plumes follow closely along the path described by the chloride center of mass.

Quantitative Estimates of Mass in Solution

The solute masses in solution were quantitated from the zeroth-moment estimation procedure described by Freyberg [this issue]. The values of the masses so obtained are summarized in Table 2. The masses of the individual compounds added to the injection solution are shown in the first row of Table 2, for comparison with the observed masses in solution. The observed masses in solution are in all cases smaller than the corresponding masses introduced into the aquifer at the beginning of the experiment, in accordance with expectations for sorbing solutes. Moreover, there is a general temporal trend for all compounds: the estimated mass in solution tends to decrease with time. This trend is particularly evident with

TABLE 2. Mass of Organic Compounds in Solution

Sampling Day	Mass, g				
	CTET	BROM	PCE	DCB	HCE
Initial*	0.37	0.38	0.36	4.0	0.23
1	0.15	0.17	not reported†	not reported†	not reported†
9	0.22	0.25	not reported†	0.69	0.03
16	0.19	0.27	not reported†	1.10	0.030
29	0.25	0.25	0.15	1.03	0.028
43	0.30	0.26	0.13	1.09	0.022
63	0.20	0.21	0.11	0.96	0.007
85	0.17	0.15	0.11	0.35	0.008
330	0.14	0.10	0.07	0.18	bdl
380	0.15	0.09	0.08	0.21	bdl
407	0.18	0.08	0.07	0.14	bdl
633	0.10	0.03	0.06	0.04	bdl
709	0.12	0.03	0.08	0.05	bdl

Mass obtained by spatial integration of synoptic sampling data. Bdl, below detection limit.

*Known mass introduced into mixing chamber.

†Not reported because of analytical artifacts.

hexachloroethane, the concentrations of which had decreased below the detection limit by the time of the eighth sampling ($t = 330$ days).

Velocities of Plume Movement

The distances traveled in the horizontal plane by the centers of mass are presented in Table 3. The positions are reported as distances in meters from the center of the injection zone. An analysis of the detailed monitoring data taken immediately after injection shows that the displacements of the initial plume positions from the center of the injection well configuration (i.e., from the origin of the coordinate system) were less than 0.3 m. Hence it is justified to assume for simplicity that the plumes were initially centered at the origin.

The faster movement of the chloride tracer plume relative to the organic solutes is manifest in the data summary in Table 3. The chloride plume traveled approximately 60 m during the

course of the 2-year experiment, an average velocity of 0.09 m/day. The fastest moving of the organic solute plumes, carbon tetrachloride (CTET), traveled a distance of only 26.6 m, less than half as far as chloride. Bromoform (BROM) was transported nearly as far as carbon tetrachloride, whereas tetrachloroethylene (PCE) and dichlorobenzene (DCB) were transported much smaller distances, 13.2 and 9.0 m, respectively. The position of the center of mass of hexachloroethane could be quantified only up to 85 days, owing to its subsequent disappearance from solution.

The distances traveled by the plume centers of mass are plotted versus elapsed time in Figure 7. The distance traveled by chloride is an approximately linear function of time, indicating constant advective velocity [Freyberg, this issue]. In contrast, all of the organic solutes exhibit decreasing velocities with increasing time, as evidenced by the curvature of the respective relationships in Figure 7.

To quantify the travel distance data (Table 3 and Figure 7) in a manner amenable to calculation of transport velocities,

TABLE 3. Distances Traveled by Plume Centers of Mass

Sampling Day	Distance from Center of Injection Zone, m					
	Cl ⁻	CTET	BROM	PCE	DCB	HCE
9	0.78	0.52	0.38	not reported*	0.24	0.42
16	1.76	1.07	0.86	not reported*	0.22	0.47
29	3.00	2.03	2.05	1.13	0.96	0.67
43	4.46	2.47	2.65	1.74	0.92	0.86
63	6.06	3.29	3.06	2.23	1.63	1.43
85	8.35	4.10	3.94	3.03	2.08	1.35
259	25.51	ns	ns	ns	ns	ns
330	ns	15.47	14.63	8.10	5.46	not reported*
380	35.74	17.26	16.39	8.72	5.75	not reported*
407	ns	18.66	17.41	8.89	6.23	not reported*
429	39.78	ns	ns	ns	ns	ns
462	42.00	ns	ns	ns	ns	ns
633	ns	24.82	21.51	12.33	8.09	not reported*
647	58.21	ns	ns	ns	ns	ns
709	ns	26.59	23.81	13.23	8.96	not reported*

Ns, not sampled.

*Not reported because of analytical interferences (PCE) or because insufficient data above detection limit (HCE).

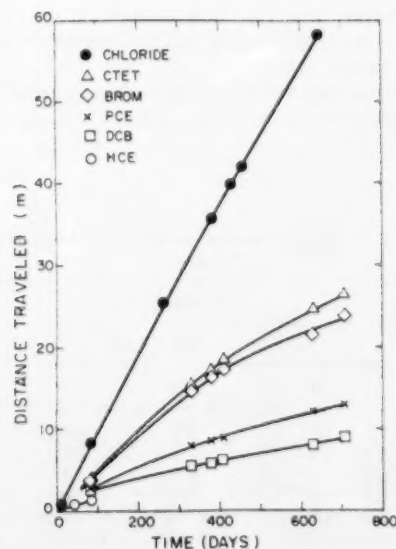


Fig. 7. Distances traveled by plume centers of mass in the horizontal plane (distances in meters).

TABLE 4. Fitting of Plume Travel Distances (m) and Velocities (m/d)

Solute	Regression Results (Equation (4))				Velocity Expression (Equation (5))
	<i>a</i>	<i>b</i>	<i>n</i>	<i>r</i> ²	
Chloride*	0.122	0.955	10	0.999	$v = 0.117t^{-0.045}$
CTET†	0.0997	0.860	10	0.997	$v = 0.086t^{-0.140}$
BROM†	0.0966	0.852	10	0.990	$v = 0.082t^{-0.148}$
PCE‡	0.0992	0.751	9	0.997	$v = 0.075t^{-0.249}$
DCB‡	0.073	0.736	9	0.988	$v = 0.054t^{-0.264}$
HCE*	0.0663	0.699	5	0.949	$v = 0.046t^{-0.301}$

Here, *n*, number of data sets used in regression.

*Obtained by fitting data for the period 16 < *t* < 647 days.

†Obtained by fitting data for the period 16 < *t* < 709 days.

‡Data for *t* = 16 days not included in regression.

*Obtained by fitting data for the period 16 < *t* < 85 days; hexachloroethane was not found in subsequent samplings.

the data were fitted to an empirical model. The model chosen as giving the best overall fit was a power-law relationship

$$D = at^b \quad (4)$$

where *D* is the distance traveled (meters) by the plume center of mass, *t* is the elapsed time (days), and *a* and *b* are empirical fitting parameters. The power law model (equation (4)) was matched to the travel distance data (Table 3) to obtain the best fit values of the parameters *a* and *b* through a least squares regression. Data corresponding to displacements less than 0.5 m were excluded from the regression because of the large relative errors inherent in such displacement estimates. The best fit values of the parameters *a* and *b* and the coefficients of determination *r*² for the individual solutes are given in Table 4. The value of *b*, the exponent of time in (4), is approximately unity (*b* = 0.955) for chloride, whereas the values of *b* are substantially smaller than unity for the organic solutes (*b* = 0.699–0.860). Alternative models for fitting the travel distance data were assessed, but were rejected for a variety of reasons. For example, a second-degree polynomial model would result for the most part in nearly as good a fit, but the form of the matching relationship leads to unrealistic conclusions regarding the initial locations of the plumes that are inconsistent with the data, and the polynomial model was therefore rejected.

The velocity dependence on time elapsed can be found by differentiating (4) with respect to time,

$$v = abt^{(b-1)} \quad (5)$$

TABLE 5. Retardation Factors Estimated From Synoptic Sampling

	Retardation Factor					
	Time, Days					
	15	30	85	250	400	650
CTET	1.8	1.9	2.1	2.3	2.4	2.5
BROM	1.9	2.0	2.2	2.5	2.6	2.8
PCE	2.7	3.1	3.9	4.8	5.3	5.9
DCB	3.9	4.6	5.7	7.3	8.0	9.0
HCE	5.1	6.1	7.9	not quantifiable*	not quantifiable*	not quantifiable*

*Not quantifiable owing to disappearance of HCE.

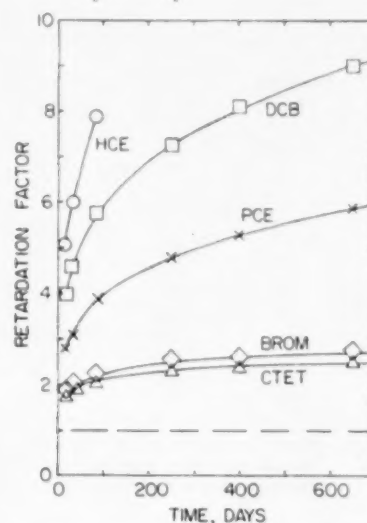


Fig. 8. Retardation factors estimated from synoptic sampling data.

where *v* is the velocity of the plume center of mass (m/day). The corresponding velocity expressions are summarized in Table 4. For all solutes, the time exponent in the velocity expression is negative; the values of the exponent for the organic solutes range from −0.140 to −0.301, compared to −0.045 for chloride. The chloride velocity is nearly constant over time, while the organic solute velocities decrease with increasing elapsed time. At the beginning of the simulated period (*t* = 16 days), the estimated velocities range from 0.103 (chloride) to 0.020 m/day (hexachloroethane). The velocities at the end of the observation period (*t* = 708 days) are found to have the following values (m/day): chloride, 0.087; carbon tetrachloride, 0.034; bromoform, 0.031; tetrachloroethylene, 0.015; and dichlorobenzene, 0.010. The organic solute plumes decelerated by a factor of 2 or more during the 2 years of the experiment, while the chloride plume decelerated by a negligible amount, about 10%.

Retardation Factors

Retardation factors *R_i* were estimated as ratios of the plume transport velocities

$$R_i = [v_{\text{chloride}}/v_i] \quad (6)$$

TABLE 6. Estimated Total Mass of Organic Compounds

Elapsed Time, days	Mass, g				
	CTET	BROM	PCE	DCB	HCE
Initial*	0.37	0.38	0.36	4.0	0.23
16	0.34	0.51	missing data	4.4	0.16
29	0.47	0.50	0.47	4.7	0.17
43	0.58	0.55	0.44	5.4	0.15
63	0.40	0.46	0.40	5.2	0.05
85	0.35	0.34	0.42	2.0	0.07
330	0.33	0.26	0.36	1.4	bdl
380	0.36	0.24	0.42	1.7	bdl
407	0.43	0.21	0.37	1.1	bdl
633	0.25	0.08	0.35	0.4	bdl
709	0.30	0.08	0.48	0.5	bdl

Bdl, below detection limit.

*Known mass introduced into injection system.

TABLE 7. Comparison of Retardation Estimates From Spatial and Temporal Data

	Temporal Data			Spatial Data	
	Retardation Factor*		Time Range,* days	Instantaneous Retardation Factor†	Ratio of Travel Distances‡
	Mean	Range			
CTET	1.73	1.6-1.8	48-119	2.0-2.1	1.8-1.9
BROM	1.70	1.5-1.8	46-122	2.1-2.3	1.9-2.0
PCE	3.30	2.7-3.9	83-217	3.8-4.7	3.0-3.7
DCB	2.73	1.8-3.7	55-245	5.2-7.2	4.0-5.6

*Retardation factor and average travel time from time-series sampling data (Table 1).

†Retardation factor from Figure 8 evaluated over the range of times given in column 4 of this table.

‡Ratio of travel distances (chloride:organic) evaluated using (4) with the parameters given in Table 4 to conform to the time interval of column 4 in this table.

evaluated at particular points in time, using the velocity expressions given in Table 4. The ratios were evaluated over the period $16 < t < 650$ days, for which reliable chloride and organic solute data were available, except for hexachloroethane, for which the data set terminated at 85 days. The times chosen for evaluation need not correspond exactly to sampling times, because the fitting procedure enables interpolation of the data.

The retardation factors estimated in this manner are given in Table 5. The retardation factor for chloride is assumed to be unity, by definition. CTET and BROM are least strongly retarded ($R = 1.8$ to 2.5 and $R = 1.9$ to 2.8 , respectively). PCE ($R = 2.7$ to 5.9) and DCB ($R = 3.9$ to 9.0) are retarded to a substantially greater degree. HCE is the most strongly retarded compound over the period for which comparison is possible ($16 < t < 85$ days), with a retardation factor approximately 30-45% greater than that of DCB during the same time period.

The estimated retardation factors increase over time for all of the organic solutes, as is illustrated in Figure 8. The retardation factors increase by an amount ranging from 40% (CTET) to 130% (DCB) over the period 16-650 days. The time dependencies of the retardation factors are qualitatively similar, as is shown in Figure 8. The rate of increase is initially rapid, then slows toward the end of the observation period. However, the retardation appears still to be increasing, albeit at a slower rate, even at the end of the nearly 2-year period.

Mass Balances

The total masses of the solutes remaining in the system were estimated by an indirect inference method, namely, by summing the mass in solution and the mass imputed to sorption on aquifer solids. The values of the mass in solution were obtained by integration over the synoptic sampling domain, and are given in Table 2. The mass imputed to sorption on solids was inferred from the retardation factor estimates (Table 5). If the sorbing solute partitions between solid and solution, the ratio between total mass and mass in solution is equal to the retardation factor [Helfferich, 1962; Snyder and Kirkland, 1974]. It follows that the total mass of the compound at a given time can be approximated as the product of the mass in solution times the retardation factor evaluated at the chosen time

where $M_{\text{tot}, i}$ and $M_{\text{sol}, i}$ are the total and dissolved masses, t is the time chosen for evaluation, and i is the solute index.

The total mass was calculated by substituting into (7) the dissolved masses, $(M_{\text{sol}, i})_t$, from Table 2 and the R_i values obtained from (6). The results of the calculations of total mass are summarized in Table 6. Shown for comparison are the total initial masses, estimated by multiplying the average measured concentrations of the injection solution times the injected volume [Mackay et al., this issue].

It is obvious from the data in Table 6 that the estimated total mass remained approximately constant for two of the organic solutes, CTET and PCE, while the total mass decreased for the other organic solutes, BROM, DCB, and HCE. For all of the organic solutes, the estimated total mass agrees within 50% with the known initial mass over the early period of observation, i.e., through day 43. Thereafter, some of the organic solutes seem to disappear from the system; first HCE, whose disappearance is observable at $t = 63$ days, followed by DCB in the sampling at $t = 85$ days and BROM in the period following $t = 300$ days. The amount of HCE had declined to nonquantifiable levels by the end of the first year, and the amounts of DCB and BROM had approached the lower margin of quantitation by the end of the second year.

DISCUSSION

This section compares the results of the time-series and synoptic sampling, presents a preliminary overall evaluation of the results in the light of prior understanding of processes likely to affect solute behavior, and suggests possible underlying phenomena or lines of explanation worthy of further exploration.

Comparison of Time-Series and Synoptic Sampling Results

The results of time-series and synoptic sampling are qualitatively consistent with regard to most major features. This consistency is important in principle, as the comparison of the results of the two kinds of monitoring is tantamount to comparing estimates based on temporal and spatial moments. These two kinds of estimators should agree when compared at similar scales.

Retardation. There is strong evidence of differential solute movement in the results of time-series monitoring, as well as in those of synoptic monitoring. This is reflected in the observed sequential breakthrough of solutes in the former case and in the observed plume separation in the latter case. These two types of observations illustrate the inherent duality of chromatographic behavior in advection-sorption systems: solutes with differing sorption affinities tend to separate in both time and space. This principle is universally accepted on the basis of chromatographic theory [Helfferich, 1962], but its experimental demonstration in groundwater field situations has been lacking.

The retardation factors estimated by the two approaches are also in fair quantitative agreement when compared on similar scales of time and distance. This can be seen by comparing the retardation factors obtained from the time-series results (Table 1) with those estimated from the spatial results (Table 5 and Figure 8). To facilitate the comparison, the ranges of retardation estimates inferred using the two approaches, at the same time scale are given in Table 7. Hexachloroethane is omitted from this assessment, because its complete disappearance confounds the analysis. The rank order of retardation factors from time-series analysis conforms to that

$$(M_{\text{tot}, i})_t = R_i (M_{\text{sol}, i})_t \quad (7)$$

from spatial analysis. However, the retardation factors from the spatial analysis are uniformly greater than those from the temporal analysis, by as much as a factor of 2 to 3.

There is a closer agreement between the temporal and spatial data when the retardation estimate from the spatial data is expressed in cumulative terms as the ratio of travel distances of the plume centers of mass (chloride:organic), shown in the last column of Table 7; the spatial values remain greater than the temporal values, but the ranges overlap in two of four cases. It may be more meaningful to compare the temporal retardation data with the ratio of travel distances from the spatial data set than with the instantaneous retardation factors from the spatial data. The temporal retardation factor represents a time average of behavior at a discrete point in space that is influenced by interactions along a flow path from the source to the point of observation. The ratio of travel distances of spatial plume centers of mass corresponds to an average of such behavior over all paths traversed, sampled at a discrete point in time, but reflecting the cumulative effect of all interactions up to that time. On the other hand, the spatial retardation factors, as estimated in this paper, represent spatial averages of instantaneous mobility; these measures are more directly related to sorptive partitioning at a given time than are the ratios of travel distances and hence more appropriate for mass balance calculations with the spatial data.

The slight quantitative differences in retardation factors inferred from the temporal and spatial data may arise from the differences in representativeness of sampling, i.e., the integral sampling of the spatial domain in the case of the synoptic sampling, in contrast to the arbitrary selection of three discrete sampling points along flow paths that may reflect local variations in aquifer properties to some extent; there are obvious manifestations of vertical heterogeneity influencing the spatial distribution of solutes [Freyberg, this issue; Mackay *et al.*, 1986]. This illustrates the kind of potentially significant integral information obtained by synoptic sampling that may justify the additional effort and expense of installing the requisite high-resolution monitoring network.

Relative mass. The results of the time-series and synoptic sampling programs also are consistent with respect to the relative mass of solutes observed. The time-series sampling shows slight excesses of carbon tetrachloride, bromoform, and tetrachloroethylene, whereas the masses of both dichlorobenzene and hexachloroethane are substantially smaller than expected (Table 1).

The spatial sampling data (Table 6) also exhibit a slight excess mass for carbon tetrachloride and tetrachloroethylene throughout the observation period, and for bromoform and dichlorobenzene during the initial period ($t < 85$ days). The mass of hexachloroethane was smaller than the initial mass from the outset of observation, the dichlorobenzene mass declined below its initial value following day 63, and the bromoform mass was depleted beginning between $t = 85$ and $t = 380$ days.

The relative masses of bromoform estimated by the two methods differ substantially. Although at first glance anomalous, the estimates are, in fact, consistent when the differences in time scale between the temporal and spatial data are considered. Evidence of the disappearance of bromoform inferred from the spatial sampling results became apparent only after a long time period, i.e., several hundred days. By that time, bromoform had already passed the time-series monitoring points from which results are reported in this paper. Bromoform's

average travel time at points a and b was 45 days (Table 1) and its concentration had declined to background levels prior to $t = 150$ days. At the farther point, c, bromoform's average travel time was greater, $t = 122$ days (Table 1), but the observed concentrations nonetheless declined to below the quantifiable limit before 250 days had elapsed. The relative total mass of bromoform observed at point c, in fact, is slightly smaller than at a and b, which suggests incipient mass disappearance at the sampling point characterized by the longest response time among the three discrete monitoring points discussed here. The overall picture reveals that the mass of bromoform was conserved during the initial part of the experiment, followed by an appreciable decrease in mass in the second year.

In the case of dichlorobenzene, the time-series sampling (Figure 3) provides corroborative evidence of the disappearance that is strikingly evident in the synoptic results (Table 6). The dichlorobenzene response at point b (Figure 3b) shows a feature that suggests rapid onset of a transformation process resulting in local disappearance of the compound. The time-series data at point b show that dichlorobenzene commenced to break through in the usual way, with the concentration below the detection limit for an initial period and then rising to appreciable levels, but following day 60 the concentration fell precipitously, and thereafter remained at negligible levels. This behavior is consistent with the conclusion based on synoptic sampling results that the dichlorobenzene mass began to decline between day 63 and day 85.

Mass Balance Interpretation

There is compelling evidence of transformation of organic solutes during the experiment. Evidence has been presented showing (1) deficiencies in mass for two compounds, dichlorobenzene and hexachloroethane, based on the time-series sampling results (Table 1) and (2) temporal declines in total mass for three compounds, bromoform, dichlorobenzene, and hexachloroethane, based on the periodic spatial sampling.

The relative total mass estimates from analysis of the synoptic sampling are summarized graphically in Figure 9. The values in Figure 9 were estimated by finding the ratio of the total mass remaining at time t to the gravimetrically determined initial mass (Table 6). The analysis suggests strongly

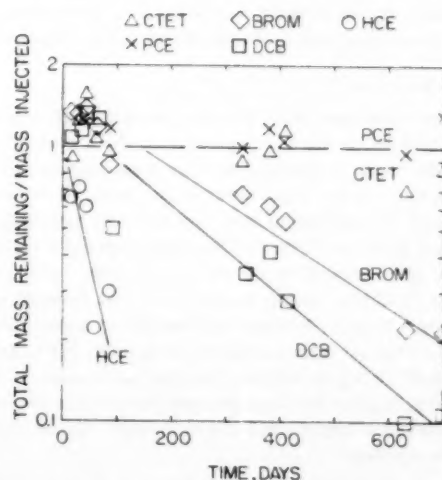


Fig. 9. Relative total mass inferred from synoptic sampling data.

TABLE 8. Summary of Mass Balance Analysis of Synoptic Data

	Relative Total Mass	
	Mean	95% Confidence Interval
Chloride	0.92	0.84-1.00
CTET	1.04	0.85-1.23
PCE	1.14	1.05-1.23
BROM		decrease to
DCB		<20% of
HCE		original mass*

Confidence interval based on standard deviation of total mass estimates from 12 spatial samplings.

*By the end of the experiment.

that bromoform, dichlorobenzene, and hexachloroethane were transformed during the course of the experiment, whereas tetrachloroethylene and carbon tetrachloride were not. The mass balance interpretation is summarized in Table 8. The means of the relative total mass estimates in Table 8 for carbon tetrachloride and tetrachloroethylene are 1.04 and 1.14, respectively, with the value for tetrachloroethylene being significantly greater than unity. In contrast, the mean relative mass for chloride is 0.92, which does not differ significantly from unity [Freyberg, this issue].

The excess of mass for carbon tetrachloride and tetrachloroethylene is nonetheless small, and conceivably stems from sampling bias. It is possible that the sampling introduces slight positive bias by drawing disproportionately large volumes of water from small-scale layers of high conductivity that are more readily permeated by the solutes, but this phenomenon would have to function selectively with the organic solutes, because there is no indication of excess mass for chloride. On the other hand, Mackay *et al.* [this issue] have shown through analysis of quality-assurance data that the analytical bias tends to be negative, yielding observed concentration values some 10% smaller than known standards, which would tend to bias the relative mass towards values smaller than unity. In any event, there is no evidence of disappearance of carbon tetrachloride and tetrachloroethylene from the system during the 2-year duration of observation.

The total masses of bromoform, dichlorobenzene, and hexachloroethane all decline to less than 20% of their original value. The disappearance of hexachloroethane commenced virtually immediately, whereas the onset of the disappearance of dichlorobenzene and bromoform was delayed by periods on the order of 100 days. The disappearance of each of these compounds, once begun, can be approximated as a first-order rate process in terms of its gross behavior, with the following rate constants: hexachloroethane, 0.02 day^{-1} ; dichlorobenzene, 0.004 day^{-1} ; and bromoform, 0.003 day^{-1} . These rate constants should be recognized as order-of-magnitude estimates, with associated uncertainties of at least a factor of 2.

Transformation Interpretation

Based on the information presented here, the disappearance of the three organic solutes characterized by declining total mass cannot be attributed with certainty to any particular mechanism. The possibility of biotransformation was recognized prior to the experiment, and indeed the solutes were selected to introduce the potential of biotransformation under a broad range of conditions, as is discussed in the first paper of this series [Mackay *et al.*, this issue]. There is some evi-

dence that all of the organic solutes in this work are potentially degradable, at least at slow rates under optimal conditions [Tabak *et al.*, 1981], but not necessarily at appreciable rates under aquifer conditions.

The general picture of slow disappearance of a solute following a substantial time lag recalls the previously published set of observations from the Palo Alto Baylands site, where chloroform and related compounds disappeared under anoxic conditions at a rate of 0.03 day^{-1} following an initial time lag of approximately 50 days [Roberts *et al.*, 1982]. In the present work the evidence is much more convincing, however, as it is based on a synopsis of data from hundreds of sampling points rather than a single point. Also, the abrupt disappearance of dichlorobenzene at point b in this work (Figure 3b) follows the pattern observed with naphthalene under aerobic conditions at the Palo Alto site [Roberts *et al.*, 1980]. Both of the latter phenomena were attributed to biotransformation. The time lags can be explained in terms of the necessity for microbial populations to increase in numbers following exposure to the substrate before compounds can be transformed at an appreciable rate [Bouwer and McCarty, 1984].

The simultaneous transformation of dichlorobenzene along with bromoform and hexachloroethane is somewhat surprising. It was presumed at the outset [Mackay *et al.*, this issue] that dichlorobenzene was likely to transform under aerobic conditions, and that bromoform, tetrachloroethylene, and carbon tetrachloride were most likely to transform under anoxic conditions; the transformation potential of hexachloroethane was unknown. At first glance, it is remarkable that the set of compounds found to disappear during the field experiment included one compound thought to be degradable under aerobic conditions (dichlorobenzene), one thought to be degradable under anoxic conditions (bromoform), and one of unknown degradability (hexachloroethane), whereas two of the compounds (carbon tetrachloride and tetrachloroethylene) thought to be degradable under anoxic conditions in fact showed no diminution of mass in the experiment. In laboratory experiments motivated by the evidence of transformation obtained from this field study, hexachloroethane has since been observed to be transformed by microorganisms under aerobic conditions and by microbes and/or abiotic agents in the presence of unsterilized Borden aquifer solids [Criddle *et al.*, 1986]. Although the dissolved oxygen concentrations in water samples from the experimental site generally are in the range of 1-5 mg/L, values at or below the detection limit are occasionally observed, and it is possible that anoxic microzones exist in which anaerobic transformation processes might occur. The degradation of these organic compounds currently is being investigated in model experiments at Stanford University and at the Robert S. Kerr Environmental Research Laboratory of the Environmental Protection Agency.

Retardation and Sorption

Evidence of retardation of organic solute movement has been presented from both time-series and spatial data. Sorption onto aquifer solids has been invoked frequently to explain the slower movement of solutes such as cations [Pickens *et al.*, 1981; Valocchi *et al.*, 1981; Dance and Reardon, 1983; Jackson and Inch, 1983] and hydrophobic organic compounds [Roberts *et al.*, 1980, 1985; Schwarzenbach *et al.*, 1983; Bouwer *et al.*, 1984] during groundwater transport in field situations. Sorptive retardation of organic solutes has been demonstrated in soil column studies by van Genuchten *et al.* [1977], Rao and

Davidson [1979]; and Schwarzenbach and Westall [1981]. The mechanism underlying sorption of hydrophobic organic compounds from aqueous solution onto aquifer solids, sediments, and soils usually is postulated to be hydrophobic partitioning into a stationary organic phase, e.g., macromolecular soil organic matter such as humic substances [Karickhoff *et al.*, 1979; Means *et al.*, 1980; Chiou *et al.*, 1983].

The organic solutes in this study are moderately hydrophobic, with octanol-water partition coefficients [Curtis *et al.*, this issue] ranging from approximately 200 for the least hydrophobic compound (bromoform) to 4000 for the most hydrophobic compound (hexachloroethane). The octanol-water partition coefficients of the other compounds are as follows: tetrachloroethylene, 400; carbon tetrachloride, 500; and dichlorobenzene, 2500. The observed retardation factors (Table 5) are greatest for the two most hydrophobic compounds, dichlorobenzene and hexachloroethane. There are minor inversions in order of the degree of retardation for the other compounds, as carbon tetrachloride is less strongly retarded relative to bromoform and tetrachloroethylene than was anticipated judging from the magnitudes of their octanol-water partition coefficients. These minor anomalies do not seriously undermine the argument that the observed retardation is caused by sorption, however, as published measurements of the octanol-water partition coefficients often vary substantially and the differences among values reported for the solutes of interest are relatively small. Furthermore, it is by no means clear that hydrophobic partitioning is the predominant mechanism of sorption of the solutes onto the Borden aquifer solids. The assumption of hydrophobic partitioning as the principal mechanism of sorption is questionable in the present case, as the organic matter fraction of the aquifer solids is quite low, i.e., $f_{oc} = 0.02\%$ [Mackay *et al.*, this issue], well below the threshold value of 0.1% believed to be the minimum to assure predominance of the organic partitioning mechanism [McCarty *et al.*, 1981; Schwarzenbach and Westall, 1981; Karickhoff, 1984].

There is independent evidence, from laboratory studies of sorption of the organic solutes onto solids excavated at the Borden site, that the retardation of the organic solutes, as estimated from the time-series sampling (Table 1), can be explained by sorption. In a subsequent paper in this series [Curtis *et al.*, this issue], the results of those sorption experiments will be presented and used to demonstrate that sorption is the main causative factor in the retardation behavior.

Long-Term Increase of Retardation

There was a marked tendency, common to all organic solutes, for the retardation factor estimated from synoptic sampling data to increase with elapsed time over the two-year observation period (Figure 8). If retardation is attributed to sorption, then a gradual increase in retardation implies a gradual temporal increase in sorption from solution onto the aquifer solids. Such a tendency might be explained in a variety of ways: (1) a directional trend of increasing sorption affinity of the aquifer solids that happens to coincide with the direction of plume movement; (2) nonlinear equilibrium sorption behavior which could lead to higher values of the distribution coefficient when solution concentrations diminish over time as a result of dispersion; (3) nonsingular sorption-desorption behavior (hysteresis) or desorption which is slow by comparison to sorption and ground water flow rate; (4) selective action of transformation processes such that the solute concentrations

at the leading edges of the organic solute plumes are diminished to a greater extent than in the trailing portions; (5) gradual increases in distribution coefficients as a result of slow approach to sorption equilibrium, e.g., owing to diffusion rate limitation.

At the time of this writing, the preponderance of evidence supports the last of the enumerated alternative explanations, i.e., that the observed increase in retardation stems from sorption rate limitation. Sorption rate experiments indicate that uptake of the organic solutes by Borden aquifer solids is remarkably slow [Curtis *et al.*, this issue] requiring on the order of at least several days to reach equilibrium, even when the solids are dispersed as in the laboratory experiments; sorptive uptake at longer times could not be quantified using the laboratory protocol of Curtis *et al.* [this issue], owing to slow losses of the volatile organic chemicals in control experiments. Additional diffusional resistance might be imposed by stratification or aggregation of the solids in their undisturbed state within the aquifer; Sudicky [this issue] has demonstrated the existence at this site of horizontal layers of low hydraulic conductivity that vary in thickness from a few centimeters to a few decimeters.

We are actively investigating such diffusional phenomena through laboratory experiments and mathematical model simulations to explain the apparent nonequilibrium behavior. To date, Goltz and Roberts [1986] have shown that the extended tailing of the organic solutes observed in time-series sampling (e.g., carbon tetrachloride and tetrachloroethylene in Figure 2) can be rationalized as an effect of diffusion limitation.

The importance of the other alternative explanations cannot be evaluated fully at this time, although work completed to date suggests they are likely to be insignificant or of secondary importance. For example, Mackay *et al.* [1986], in a discussion of the ongoing efforts to characterize the spatial variability of sorption characteristics, presented preliminary evidence that there is no apparent trend, in the horizontal direction, in the average sorption characteristics of the aquifer solids within the depth interval traversed by the solute plumes (alternative 1). Van Genuchten and Wierenga [1976] have proven that increasing retardation, resulting from either nonlinear or nonsingle-valued sorption equilibrium, can lead to temporal changes in retardation of the kind observed here (alternatives 2 and 3, respectively). However, Curtis *et al.* [this issue] have shown that the sorption isotherms from 3-day equilibration batch experiments with Borden sand are approximately linear, with no significant hysteresis. Current hypotheses regarding biotransformation in subsurface environments would suggest that alternative 4 is unlikely; in fact, the reverse might be expected, i.e., that biotransformation of the trailing edges of the plumes would be more rapid because the native microorganisms capable of transforming a particular compound (presumed to be attached to the aquifer solids) would have had more time to multiply or acclimate to the compound [Bouwer and McCarty, 1984]. The temporal data provide one striking example of solute disappearance at the trailing edge (DCB in Figure 3b), and there was no evidence of greater organic solute disappearance at the front edges of the spatial plumes. Furthermore, the organic solutes show similar increases in retardation over time (Figure 9), regardless of whether their total mass is conserved or diminishes (Table 6).

To the extent that the temporal increase in retardation truly represents nonequilibrium behavior, the quasi-equilibrium analysis presented in this paper is not strictly correct. In par-

ticular, the validity of the mass balance computation by imputing the sorbed mass would be affected by deviations from local equilibrium. Moreover, it must be recognized that the temporal behavior of the retardation factors may be influenced by the spatial variability of the porous medium. Further work in characterizing the porous medium and its interaction with organic solutes, as well as in modeling transport behavior, is needed.

SUMMARY AND CONCLUSION

The experimental results described here represent the most extensive, high-resolution data set yet obtained to aid in understanding organic solute transport in ground water. Transport of five organic solutes, differing appreciably in terms of sorption and transformation behavior, has been characterized over a 2-year period in a spatial domain that ultimately encompassed approximately 1000 m³ of porous medium.

The transport of organic solutes was retarded to varying degrees relative to chloride (retardation factors ranging from 2 to 10), in rough accord with the solutes' hydrophobicities. The retardation factors increased with elapsed time in a manner that suggests deviation from local equilibrium. Concomitantly, the mass in solution, estimated by integrating over the spatial sampling domain, declined for all organic solutes. Mass balances, accounting for the dissolved amounts and, by an indirect estimation technique, the sorbed amounts, showed the mass declining for three of the compounds (bromofom, dichlorobenzene, and hexachloroethane) over the course of the experiment, while mass was conserved for the remaining two compounds (carbon tetrachloride and tetrachloroethylene). The retardation behavior of the residual amounts of the transforming solutes was similar to that of solutes whose mass was conserved. The evidence of retardation and transformation was largely consistent between the time-series and spatial monitoring programs; where differences arise, these probably can be explained by local heterogeneities. Heterogeneity notwithstanding, the gross behavior of the solute plumes appears amenable to description with transport models that treat the porous medium as a quasi-homogeneous continuum, accounting properly for advection, dispersion, sorption, transformation, and diffusion. The data presented here will provide opportunities for calibration and verification of such transport models.

Although arduous, transport experiments such as described here offer the advantage of yielding direct evidence of long-term transport behavior of organic solutes under natural conditions. Requisite for success are adequate prior characterization of the site; careful, quantitative control during introduction of the solutes; detailed spatial and temporal monitoring of solute concentrations; careful implementation of the experimental plan in the field and in the laboratory, with systematic quality assurance checks; and thoughtful interpretation of the data at intermediate points during the course of the experiment, modifying the plan to take advantage of unforeseen opportunities and to assure efficient use of the sampling and analytical effort.

Acknowledgments. Gary Hopkins contributed greatly to the design and implementation of the field experiment, including the development of the organic solute sampling and analytical procedures, the conduct of the quality assurance program and the preliminary interpretation of the monitoring data. Stephanie O'Hannesin (University of Waterloo), who directed the organics sampling effort in the field, designed and implemented critical aspects of the sample tracking and quality control programs. The moment estimation was performed

by David Freyberg with the assistance of Elizabeth Bradley, Amy Chen, Jeff Davis, Pat Fennessy, David Leib, and Karen Murphy. Although the information described in this article has been funded in part by the United States Environmental Protection Agency under Assistance Agreement CR-808851 to Stanford University, it has not been subjected to the Agency's required peer and administrative review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

REFERENCES

- Bouwer, E. J., and P. L. McCarty, Modeling of trace organics biotransformation in the subsurface, *Ground Water*, 22(4), 433-440, 1984.
- Bouwer, E. J., P. L. McCarty, H. Bouwer, and R. C. Rice, Organic contaminant behavior during rapid infiltration of secondary wastewater at the Phoenix 23rd Avenue project, *Water Res.*, 18(4), 463-472, 1984.
- Chiou, C. T., P. E. Porter, and D. W. Schmedding, Partition equilibria of nonionic organic compounds between soil organic matter and water, *Environ. Sci. Technol.*, 17, 227-231, 1983.
- Criddle, C. S., P. L. McCarty, M. C. Elliott, and J. F. Barker, Reduction of hexachloroethane to tetrachloroethylene in groundwater, *Contam. Hydrol.*, 1(1), 133-142, 1986.
- Curtis, G. P., M. Reinhard, and P. V. Roberts, A natural gradient experiment on solute transport in a sand aquifer, 4, Sorption of organic solutes and its influence on mobility, *Water Resour. Res.*, this issue.
- Dance, J. T., and E. J. Reardon, Migration of contaminants in groundwater at a landfill: A case study, 5, Cation migration in the dispersion test, *J. Hydrol.*, 63, 109-130, 1983.
- Freyberg, D. L., A natural gradient experiment on solute transport in a sand aquifer, 2, Spatial moments and the advection and dispersion of nonreactive tracers, *Water Resour. Res.*, this issue.
- Goltz, M. N., and P. V. Roberts, Diffusion of sorbing solutes—Impact on contaminant transport in ground water, *Contam. Hydrol.*, 1(1), 77-94, 1986.
- Hashimoto, I., K. B. Deshpande, and H. C. Thomas, Peclet numbers and retardation factors for ion exchange columns, *Ind. Eng. Chem. Fundam.*, 3(3), 213-218, 1964.
- Helfferich, F., *Ion Exchange*, McGraw-Hill, New York, 1962.
- Hunt, B., Dispersive sources in uniform ground-water flow, *J. Hydraul. Div. Am. Soc. Civ. Eng.*, 104(HY1), 75-85, 1978.
- Jackson, R. E., and K. J. Inch, Partitioning of strontium-90 among aqueous and mineral species in a contaminated aquifer, *Environ. Sci. Technol.*, 17(4), 231-237, 1983.
- Karickhoff, S. W., Organic pollutant sorption in aquatic systems, *J. Hydraul. Eng.*, 110(6), 707-735, 1984.
- Karickhoff, S. W., D. S. Brown, and T. A. Scott, Sorption of hydrophobic pollutants on natural sediments, *Water Res.*, 13, 241-248, 1979.
- Lapidus, L., and N. R. Amundson, Mathematics of adsorption in beds. VI. The effect of longitudinal diffusion in ion exchange and chromatographic columns, *J. Phys. Chem.*, 56, 984-988, 1952.
- Lindstrom, F. T., R. Haque, V. H. Freed, and L. Boesma, Theory on the movement of some herbicides in soils: Linear diffusion and convection of chemicals in soils, *Environ. Sci. Technol.*, 1(7), 561-565, 1967.
- Mackay, D. M., W. P. Ball, and M. G. Durant, Variability of aquifer sorption properties in a field experiment on groundwater transport of organic solutes: Methods and preliminary results, *Contamin. Hydrol.*, 1(1), 119-132, 1986.
- Mackay, D. M., D. L. Freyberg, P. V. Roberts, and J. A. Cherry, A natural gradient experiment on solute transport in a sand aquifer, 1, Approach and overview of plume movement, *Water Resour. Res.*, this issue.
- McCarty, P. L., M. Reinhard, and B. E. Rittman, Trace organics in groundwater, *Environ. Sci. Technol.*, 15(1), 40-51, 1981.
- Means, J. C., S. G. Wood, J. J. Hassett, and W. L. Banwart, Sorption of polynuclear aromatic hydrocarbons by sediments and soils, *Environ. Sci. Technol.*, 14(12), 1524-1528, 1980.
- Pickens, J. F., R. E. Jackson, K. J. Inch, and W. F. Merritt, Measurement of distribution coefficients using a radial injection dual-tracer test, *Water Resour. Res.*, 17(3), 529-544, 1981.
- Rao, P. S. C., and J. M. Davidson, Adsorption and movement of selected pesticides at high concentrations in soils, *Water Res.*, 13, 375-380, 1979.
- Roberts, P. V., P. L. McCarty, M. Reinhard, and J. Schreiner,

- Organic contaminant behavior during groundwater recharge, *J. Water Pollut. Control Fed.*, 52(1), 161-172, 1980.
- Roberts, P. V., J. E. Schreiner, and G. D. Hopkins, Field study of organic water quality changes during ground water recharge in the Palo Alto Baylands, *Water Res.*, 16, 1025-1035, 1982.
- Roberts, P. V., M. Reinhard, G. D. Hopkins, and R. S. Summers, Advection-dispersion models for simulating the transport of organic contaminants, in *Groundwater Quality*, edited by C. H. Ward, W. Giger, and P. L. McCarty, John Wiley, New York, 1985.
- Schwarzenbach, R. P., and J. Westall, Transport of nonpolar organic compounds from surface water to groundwater, Laboratory sorption studies, *Environ. Sci. Technol.*, 15(11), 1360-1367, 1981.
- Schwarzenbach, R. P., W. Giger, E. Hoehn, and J. K. Schneider, Behavior of organic compounds during infiltration of river water to groundwater, Field studies, *Environ. Sci. Technol.*, 17, 472-479, 1983.
- Snyder, L. R., and J. J. Kirkland, *Introduction to Modern Liquid Chromatography*, 534 pp., John Wiley, New York, 1974.
- Sudicky, E. A., J. A. Cherry, and E. O. Frind, Migration of contaminants in groundwater at a landfill: A case study, 4, A natural-gradient dispersion test, *J. Hydrol.*, 63, 81-108, 1983.
- Tabak, H. H., S. A. Quave, C. I. Mashni, and E. F. Barth, Biodegradability studies with organic priority pollutants, *J. Water Poll. Control Fed.*, 53(10), 1503-1518, 1981.
- Valocchi, A. J., R. L. Street, and P. V. Roberts, Transport of ion-exchanging solutes in groundwater: Chromatographic theory and field simulation, *Water Resour. Res.*, 17, 1517-1527, 1981.
- Van Genuchten, M. Th., and P. J. Wierenga, Mass transfer studies in sorbing porous media, I, Analytical solutions, *Soil Sci. Soc. Am. J.*, 40(4), 473-478, 1976.
- Van Genuchten, M. Th., P. J. Wierenga, and G. A. O'Connor, Mass transfer studies in sorbing porous media, III, Experimental evaluation with 2, 4, 5, -T, *Soil Sci. Soc. Am. J.*, 41(2), 278-285, 1977.
- Vermeulen, T., and N. K. Hiestler, Ion exchange chromatography of trace components, *Ind. Eng. Chem.*, 44, 636-650, 1952.
- Yu, C., W. A. Jester, and A. R. Jarrett, Simultaneous determination of dispersion coefficients and retardation factors for a low level radioactive waste burial site, *Radioact. Waste Manage. Nucl. Fuel Cycle*, 4(4), 401-420, 1984.
- M. N. Goltz, D. M. MacKay, and P. V. Roberts, Department of Civil Engineering, Terman Engineering Center, Stanford University, Stanford, CA 94305.

(Received June 24, 1985;
revised April 9, 1986;
accepted April 21, 1986.)

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

This article documents research that was conducted under the auspices of the U.S. Environmental Protection Agency (USEPA). As an arm of the government, the USEPA has a paid up, non-exclusive, irrevocable, worldwide license to reproduce, prepare derivative works, and distribute to the public all of the material contained herein, and to grant others acting on its behalf the right to do so. The USEPA grants to the National Technical Information Service, Department of Commerce, the right to act as its agent in the distribution of this material.